Determining the composition of ammonia/water mixtures using short-wave near-infrared spectroscopy

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ABSTRACT

This paper proposes a methodology based on short-wave near-infrared spectroscopy to determine the ammonia content of ammonia/water mixtures with ammonia mass fraction in the range 0.35–0.65. Establishing this methodology meant modeling the relationship between the pressure bar (15–25) bar, temperature (20–50) °C and composition of the ammonia–water in the mixture (0.35–0.65 in ammonia mass fraction) with absorbance at 1033 nm. The experiments were designed to optimize experimental work. A 2^3 factorial design+3 center points was used to establish and analyze the significance of the variables in the absorbance using analysis of variance (ANOVA). A linear model for absorbance was obtained using the least squares method. The trueness of the results versus the values obtained was assessed using a reference method; density measurement was chosen for this study. The accuracy of the results in terms of root-mean-square deviation (RMSD) was 3.7%. The methodology proposed represents a fast alternative for the "in-situ" measurement of the ammonia composition of ammonia–water mixtures in absorption refrigeration systems.

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1. Introduction

The ammonia/water mixture is a conventional working pair in absorption refrigeration cycles [1]. In these systems ammonia is the refrigerant while water is the absorbent. Since the first patent for an absorption refrigeration system operating with ammonia/water [2], many efforts have been made to optimize the design of the different parts of the system (condenser, evaporator, absorber and generator) and improve the working fluids [3,4]. An important issue when a prototype is being studied, and in the common control of an absorption machine, is the measurement of the various properties of the working fluid, such as temperature, pressure and composition. The first two are easily measurable using conventional RTD or thermocouples and pressure gauges or transmitters. However, determining the composition is not so simple. The most common way of doing this in absorption refrigeration systems is by the titration method. The accuracy of this is quite high, but it is time-consuming and requires sampling to be measured externally [5]. An alternative is the use of "in-situ" measurement systems, such as the Coriolis mass flow meter, which can determine the density of the fluid, and knowing temperature and pressure means the composition can be determined by a previous calibration [6].

In recent years a number of studies describing various types of ammonia sensor have been published [7], but these focus on determining trace quantities of ammonia. Ammonia in water samples can be measured by EPA test methods [8] and several companies have developed on-line ammonia analyzers based on these standard methods [9,10]. However, as far as we know the applications described are not considered for use in the experimental conditions of pressure and temperature required to analyze ammonia/water mixtures with high ammonia content.

Near-infrared (NIR) spectroscopy is one of the more commonly used techniques for the in-situ analysis of samples. This technique is non-destructive, the measurements are nearly instantaneous and real time data can be obtained. Analytical methodologies based on the univariate and multivariate calibration of NIR spectra data are being used in several fields: agro-food [11,12] pharmaceutical [13] and refining [14–16]. In recent years infrared spectroscopy techniques associated with multivariate data analysis using linear or nonlinear algorithms have proven to be powerful tools in the analysis of fuel samples, such as gasoline, diesel, alcohol fuel, and bio-oil [17–26].

The potential of NIR spectroscopy in determining ammonia in ammonia/water mixtures was considered by the authors in a previous paper [27]. The experiments were carried out on mixtures with up to 28% ammonia mass fraction at room temperature and atmospheric pressure in the (1100–2400) nm spectral region.

Two intense bands around 1500 nm and 2008 nm associated with the combination bands of the stretching vibration of N–H groups can be detected in this region. However, the authors established that a loss of sensitivity in the detector was observed in ammonia mass fractions higher than 10%.

Over the last few years it has been reported that the high transmittance of light in the spectral region of the short-wave near-infrared (SW-NIR), from 700 nm to 1100 nm, together with a lessening of the problem caused by the intense water absorption band in the long-wave NIR spectral region [28], is very suitable for the on-line analysis of complex samples [29–33]. Some applications in this spectral region have been reported to determine major compounds in food [34–36]. To the best of our knowledge only two papers have been published that give an insight into the potential of the short-wave NIR region for analyzing ammonia in sample liquids [37,38]. One [37] focuses on exploring the differences between the spectra of pure water versus the spectrum of water–ammonia obtained at atmospheric pressures and at room temperature, while the other [38] reports the evanescent detection of gas ammonia using a fiber-optic with two forms of dye.

The present study reports a method based on SW-NIR spectroscopy to determine the ammonia content in ammonia/water mixtures with high ammonia mass fraction (0.35–0.65). This methodology can be usefully incorporated into the "in-situ" analysis of the mixture in absorption refrigeration systems.

Using this method means correlating the infrared spectra of the samples with the experimental factors involved. In the area of application, working with liquid ammonia/water mixtures requires the use of moderate pressure (between 2 and 30 bar) and temperature (up to 130 °C), and both variables can affect the spectroscopic measurement [39]. It is therefore important to optimize the experiments required for establishing the regression model. In the present study the relationship between the absorbance of the mixture at 1033 nm, temperature, pressure and ammonia mass fraction is established using experimental design techniques [40]. The experiments were designed following a 2^3 full factorial design with three center points in order to assess the absence of curvature. The ammonia mass fraction range considered was from 0.35 to 0.65, which includes the conventional composition of the ammonia/water working pair currently used in absorption refrigeration systems. The experimentation was carried out using a homemade stainless steel cell designed to withstand high pressures and temperatures.

Absorbance at 1033 nm was used as a means of obtaining linear regression models using the least-squares method. The significance of the temperature and pressure and the effect of their interaction on the absorbance was evaluated by analysis of variance (ANOVA) [41].

The trueness and accuracy [41] of the model were also evaluated. The trueness was assessed by comparison with an alternative technique; the density measurement of the ammonia/water mixture was chosen [6] for this study. Accuracy was evaluated in terms of root mean squares deviation (RMSD) through an analysis of 17 new representative samples.

2. Experimental

2.1. Chemicals

For the preparation of the mixtures, liquefied ammonia gas supplied by Carburos Metálicos (purity > 99.98%) and ultrapure-Q water were used. Dry nitrogen (Messer, purity > 99%) was used to pressurize the measuring cell.
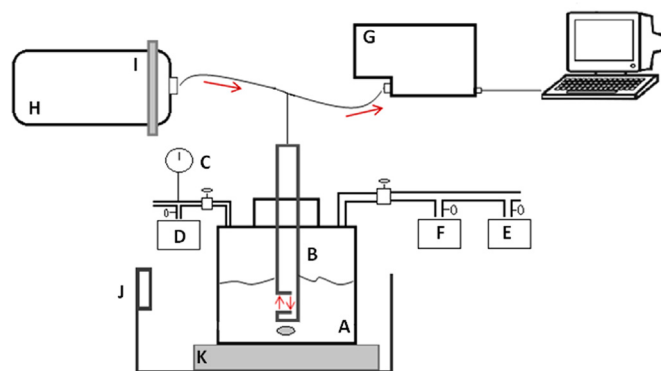

Fig. 1. Instrumental configuration. (A): Measuring cell. (B): Optical probe. (C): Pressure manometer. (D): Dry nitrogen. (E): Ammonia gas. (F): Vacuum pump. (G): Spectrophotometer. (H): Light source. (I): Filter. (J): Thermostatic bath. (K): Magnetic stirrer.

2.2. Experimental setup and spectrum

Fig. 1 shows a scheme of the experimental setup. This setup comprises a measuring cell (A) with the NIR probe (B), a pressure manometer (C) connected to a nitrogen cylinder (D), an auxiliary cylinder to introduce the ammonia (E), and a vacuum pump (F). The NIR probe consists of an industrial optic fiber probe with a pathlength tip of 10 mm, connected to a Maya 2000 Pro Vis-NIR spectrophotometer (G) with a HL-2000-CAL tungsten halogen light source (H) and a high-pass filter (> 590 nm) (I). The spectrophotometer is connected to a computer for data acquisition.

To carry out the experiments, a 150 mL stainless steel measuring cell was designed and built to withstand pressures of up to 2 MPa. This cell has three openings at the top. The central opening is used to introduce the optical probe, the second is used to introduce the components (water and ammonia), while the third is used to pressurize and empty the cell. The experimental procedure to prepare the ammonia–water in the cell is as follows. First of all the water content is introduced into the cell using a syringe. The mass of water is determined using analytical scales (Mettler Toledo, mod. PR2003DR, resolution 0.1 mg). The desired quantity of ammonia is then introduced directly into an auxiliary cylinder using liquid nitrogen to ease the sampling. The mass of ammonia in the cylinder is determined using scales (Mettler Toledo, mod. ME2002, resolution 0.01 g). Next the auxiliary cylinder is connected to the measuring cell immersed in ice and the valve is opened. The cylinder is heated to ensure that the maximum quantity of ammonia passes into the cell. Finally, the mass of ammonia remaining in the cylinder is again measured on the scales to determine by difference the quantity of ammonia inside the cell.

When the sample is ready, the cell is put into a thermostatic bath (Lauda, mod. E106T) (J) to control the temperature of the experiment and then connected to the nitrogen line through a spiral-shaped tube. The purpose of this is to pressurize the cell to keep the samples liquid. The samples are stirred constantly (K).

The pure water spectrum was recorded before each measurement in order to establish the blank signal. For each sample analyzed, a spectrum of between 997.6 nm and 1065 nm was acquired using the Maya2000 Pro software VIS NIR spectrophotometer. The data vector contains 155 values relating to the absorbance recorder each 0.4383 nm. The NIR spectra were exported and converted into a MATLAB file for pretreatment before acquiring the intensity absorption value at 1033 nm.